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BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

No. 17

THE FUNCTION OF TIME IN THE VITRIFICATION OF CLAYS

BY

G. H. BROWN, Assistant Ceramic Chemist

and

G. A. MURRAY, Laboratory Assistant

Bureau of Standards

[MAY 20, 1913]



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1. INTRODUCTION

(a) **General Statement.**—It is a well-known fact that time is an exceedingly important factor in the maturing of clays and bodies. A certain result may be obtained either by the use of a higher temperature for a shorter time or a lower temperature for a longer time. This fact we see constantly illustrated in the firing of all kinds of clay products, the melting of glass, the softening of pyrometric cones, etc. Yet there are definite thermal limits to which such relations are confined. These correspond to the lowest temperature at which partial softening, which is a necessary condition of vitrification, can take place.

It should be recognized also that the closing up of the pore system is not entirely due to the action of fluxes. Part of it is undoubtedly to be ascribed to the contraction of the colloidal portion of clays, since condensation is typical of many amorphous

bodies, such as pure alumina, magnesia, zirconia, etc. We have, however, no means of differentiating between the two kinds of contraction. In impure clays and in materials like shales this condensation is not marked. The colloidal material causing the contraction in question is active in this direction only as long as it persists in this form. As soon as it becomes transformed into the crystalline state or becomes "set," due to the action of fluxes, it ceases to show this phenomenon. The addition of colloidal silicic acid to clay, therefore, does not increase the shrinkage, for the reason that upon loss of the chemical water and further ignition the substance becomes transformed into crystalline silica.

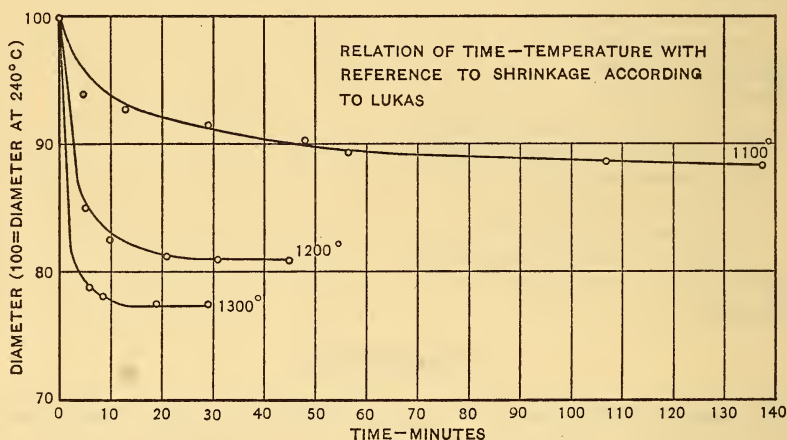


Fig. 1

(b) **Previous Work.**—Very little work has been done in connection with the effect of time upon the condensation and vitrification of clays. Lukas¹ determined the contraction suffered by small specimens of Zettlitz kaolin. In Fig. 1 the results of his measurements are plotted, showing the different rates at which the condition of apparent equilibrium is reached, as well as the rate at which the pore space is closed at different temperatures. With regard to the first point, it is seen that at higher temperatures constancy in porosity is approached most rapidly; with reference to the second, it is clearly shown that, as is to be expected, higher temperatures cause the shrinkage to be greater.

¹ Zs. f. Physik. Chemie, 52, p. 327.

The increase in shrinkage becomes smaller as the temperature rises. Thus, while the gain in shrinkage between 1100° and 1200° C is quite large, it is very much smaller between 1200° and 1300° . At still higher temperatures the values would tend to coincide more and more.

Mellor¹ has correlated the time effect by refiring a porcelain body repeatedly at cone 8. He finds that the rate at which the contraction takes place may be represented by an expression similar to that for the speed of a bimolecular reaction. According to this finding "the change of contraction during each firing

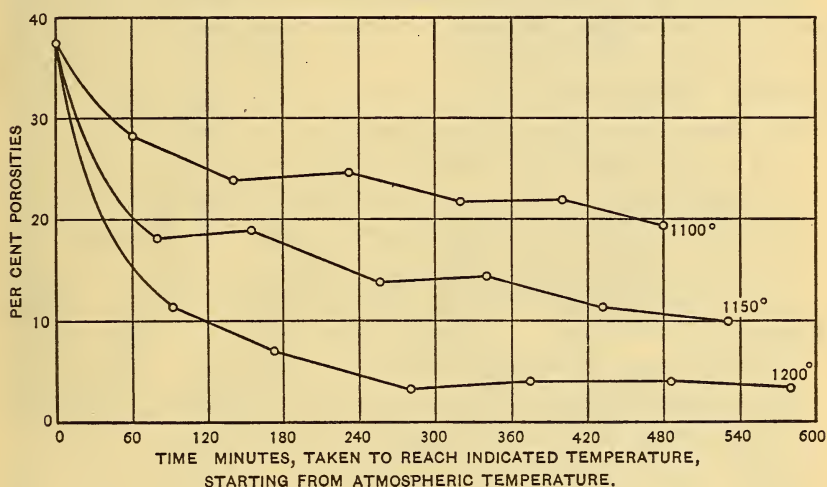


Fig. 2

is proportional to the square of the contraction which is yet to be made." This, of course, is but a coincidence.

Bleining and Boys² fired small brick specimens made from a paving-brick shale, previously ignited and oxidized at 650° C at six rates to a maximum temperature of 1200° C. The rates of the six heating schedules varied from 2.05° to 16° per minute. The firing was done in a platinum resistance furnace. In Fig. 2 the results of this work are presented. An examination of these curves shows that the drop in porosity, or the rate of vitrification, is very much greater at the beginning of the heating and gradually diminishes as it is continued. Thus, during the first 72 minutes

¹ Transactions English Ceramic Soc., 9, p. 79.

² Trans. Am. Ceramic Soc., 13, p. 387.

the rate of vitrification is about 7.5 times as great as that between 72 and 174 minutes, reduced to porosity drop per minute. Considering points of equal porosity, it is observed, for instance, that a porosity of 20 per cent is obtained at 1100° after 480 minutes, while the same point is reached in a 68-minute run up to 1150° and in considerably less time in the 1200° firing. Similarly, 10 per cent porosity is reached in a 72-minute run to 1200° and after 536 minutes up to 1150° .

2. DESCRIPTION OF WORK

The plan of the present work followed was that of Bleininger and Boys, consisting in heating clays to their maturing temperatures at definite rates and comparing the heat effect by means of porosity and shrinkage determinations. Six clays were studied in this connection, which were as follows:

1. A paving-brick shale from Streator, Ill. (Lab. No. 30).
2. A paving-brick shale from Cleveland, Ohio (Lab. No. 16).
3. A paving-brick shale from Canton, Ohio (Lab. No. 35).
4. A red burning surface clay from Urbana, Ill. (Lab. No. 37).
5. A calcareous, buff burning surface clay, Heron Lake, Minn. (Lab. No. 14).
6. A No. 3 fire clay, West Decatur, Pa. (Lab. No. 12).

The chemical analyses of these materials are given in Table 1.

TABLE 1

	Clay No. 1	Clay No. 2	Clay No. 3	Clay No. 4	Clay No. 5	Clay No. 6
SiO ₂	58.98	57.75	57.30	73.06	55.22	60.41
Al ₂ O ₃	19.59	22.30	24.31	12.36	11.88	19.49
Fe ₂ O ₃	7.46	6.51	3.30	2.26	4.37	2.07
TiO ₂76	.86	.98	.78	.95	1.98
CaO.....	.95	1.75	.58	.83	8.62	.42
MgO.....	1.55	.08	2.19	1.27	2.66	.56
Na ₂ O.....	1.08	.81	1.11	.97	.80	1.35
K ₂ O.....	2.27	3.43	2.43	2.10	1.48	2.76
Loss at 100°.....	.29	.78	.98	1.3448
Loss on ignition.....	7.18	6.01	6.93	5.11	13.94	10.84
Total.....	100.11	100.28	100.11	100.08	99.92	100.36

The clays were ground in the dry pan, screened, and tempered in the pan to a homogeneous mass of good plastic consistency.

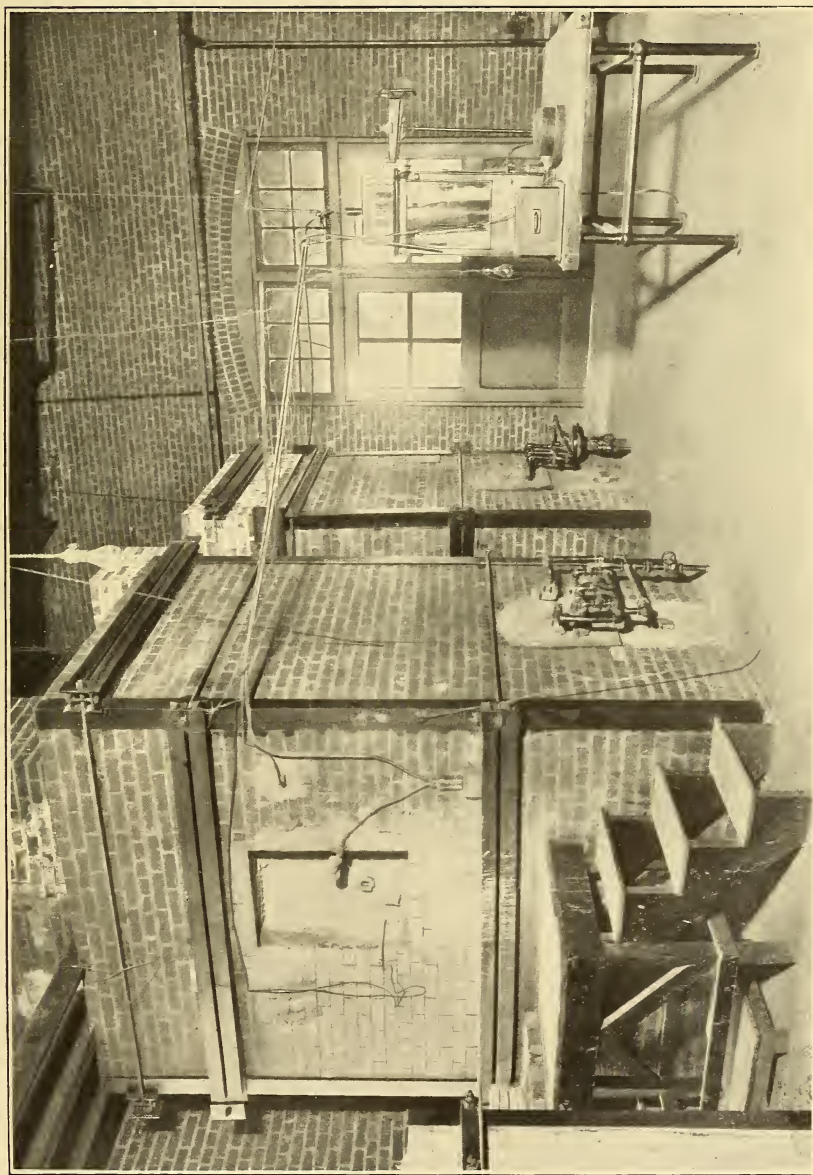


Fig. 3.—View of the kiln used

These plastic batches were then put through a small auger machine and pressed into a cylindrical column $2\frac{3}{4}$ inches in diameter. This was then cut into disks 1 inch in thickness. After drying the specimens they were fired in a gas-fired kiln to 850° C. This temperature was maintained until the clays were fully oxidized.

The volume of the pieces was then determined by means of the Seger voluminometer as was the porosity. Following this they were thoroughly dried and subjected to firings arranged according to definite schedules. The burning was carried on in a large down-draft test kiln, fired with natural gas. Accurate temperature control was maintained by means of a recording Siemens-Halske pyrometer, checked by readings from another thermocouple connected to a nonrecording millivoltmeter. The draft was regulated according to a delicate manometer and a recording carbon dioxide apparatus. Pyrometric cones were placed in the kiln for each burn.

In Fig. 3 the kiln used for this work is shown. Owing to the precautions taken it was quite an easy matter to follow the straight lines of the time-temperature schedules with considerable accuracy. The rates of firing as first planned were as follows:

Temperature increase in $^{\circ}$ C per hour..	50	42.5	35	27.5	20
Duration of burn, in hours	24	26	32	44	60

It was found, however, after making a number of runs, that this arrangement was unsatisfactory, owing to the short intervals in the duration of the burns, and for this reason a second schedule was adopted:

Temperature increase in $^{\circ}$ C per hour.....	50	25	16.6	12.5
Duration of burn, in hours	24	48	72	96

At intervals of 20° during the vitrification stage of the clays two disks were drawn of every clay through an opening in the kiln door and allowed to cool in a small pot furnace, previously heated to about 800° . Determinations of the volume, porosity, and apparent specific gravity were made of each disk.

3. DISCUSSION OF RESULTS

(a) Clay No. 1.—In Table 2 the results of the porosity and shrinkage measurements are compiled, which are plotted in the diagrams of Figs. 4 and 5.

TABLE 2
Clay No. 1 (Lab. No. 30)

Temperature reached, °C	Rate of heating, °C per hour							
	42.5	27.5	20.0	12.5	42.5	27.5	20.0	12.5
	Per cent porosity				Per cent volume shrinkage			
1070.....	26.1	25.6	22.9	16.8	7.8	9.6	13.0	17.7
1090.....	22.6	19.9	20.6	12.5	11.6	14.8	14.6	19.7
1110.....	20.1	15.8	12.3	9.2	13.9	17.9	20.2	21.3
1130.....	15.5	10.5	9.5	7.3	18.4	21.4	22.2	16.9
1150.....	8.9	6.9	5.5	15.4	22.2	22.0	20.9	12.6
1170.....	7.6	6.8	18.6	20.5	22.2	16.6	8.0	9.2
1190.....	7.3	17.9	23.7	19.4	6.8	3.8	1.8
1210.....	19.8	21.3	6.8	2.7

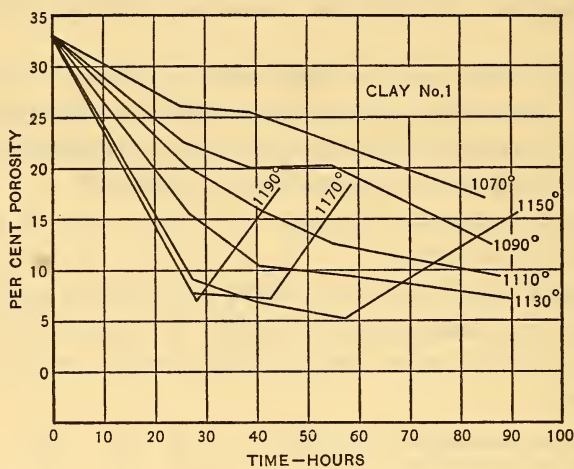


Fig. 4

From these the following iso-porosity relations are found to hold:

Porosity	Temperature reached	Time	Porosity	Temperature reached	Time
Per cent	°	Hours	Per cent	°	Hours
20	1070	69	15	1110	42.5
20	1090	39	15	1130	18
20	1110	26	10	1110	80
15	1090	75	10	1130	47

Overburning begins at 1150° after 57.5 hours, at 1170° after 43 hours, and 1190° after 28 hours. A state of equilibrium was not reached in any case, since the curves for the temperature 1070° to 1130° still show a decided slope, and it is reasonable to suppose that the minimum porosity would be reached at 1130° , 1110° , and perhaps 1090° after increasing periods of time. The suddenness of overburning is somewhat surprising, and it is evident that the rapidity of the vesicular structure development is both a function of the temperature and rate of firing. Overburning is not merely a question of temperature but of time as well, since at the same temperature both a sound or a poor structure may be obtained, depending simply upon the rate of firing. For the clay

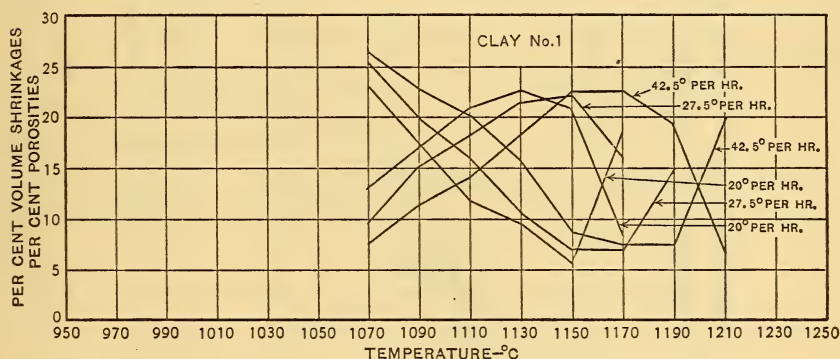


Fig. 5

in question it would undoubtedly be better to complete the burning at 1130° at a slow rate of heating. The practice of "soaking" a kiln therefore is of value, provided that the heat treatment is well within the critical temperature range.

The diagram of Fig. 5 makes possible the comparison of the shrinkage and porosity curves. The peculiar fact is at once noted that the points of minimum porosity and maximum shrinkage are not coincident. Thus the curve representing the heating rate of 20° per hour shows maximum shrinkage at 1130° and minimum porosity at 1150° . The same thing holds also for the other curves.

This tends to show that vesicular structure exists and that closed cavities are formed into which water can not penetrate

and which for this reason escape observation in the usual porosity determination. The shrinkage curves again indicate the fact that slow firing matures the clay at a lower temperature than more rapid heating, since the 20° rate results in maximum condensa-

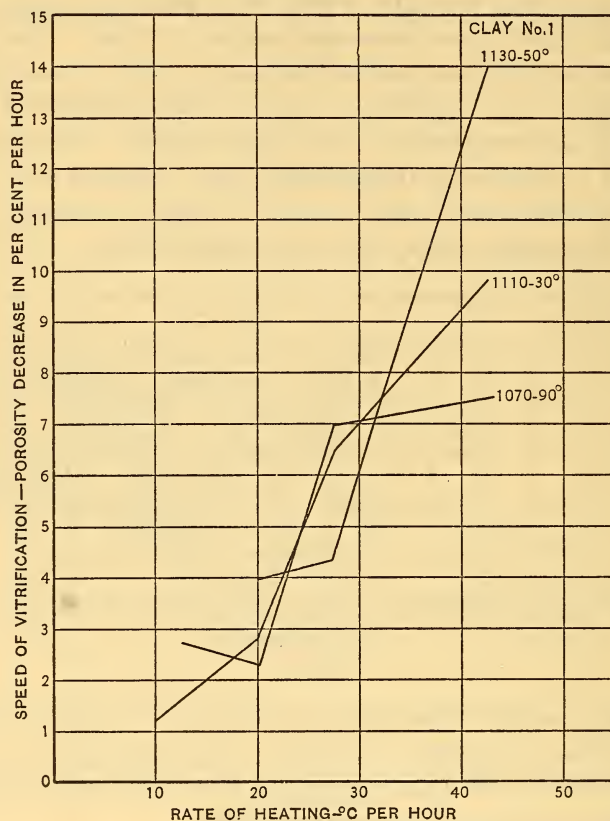


Fig. 6

tion at 1130°, while the others correspond to 1150° and 1170°, respectively.

By calculating the porosity decrease, expressed in per cent per hour, and comparing this with the rate of firing the speeds of vitrification are computed. These are shown in Fig. 6. As is to be expected, the greatest speed of contraction is obtained by the most rapid heating. As the lower porosities are reached the rate of vitrification diminishes. The rate of contraction, however, is

not a simple function of the heat increment, but is complicated by the degree of viscosity of the softening mass and is in part rendered unreal by the development of vesicular pore space. It is obvious from the results obtained that the rate of 42.5° per hour is entirely too fast for obtaining a sound structure. Slow burning to the minimum temperature will produce the best results with this clay.

(b) Clay No. 2.—The numerical results of the porosity and shrinkage determinations are collected in Table 3, and the diagram of the porosity-time-temperature relations is given in Fig. 7.

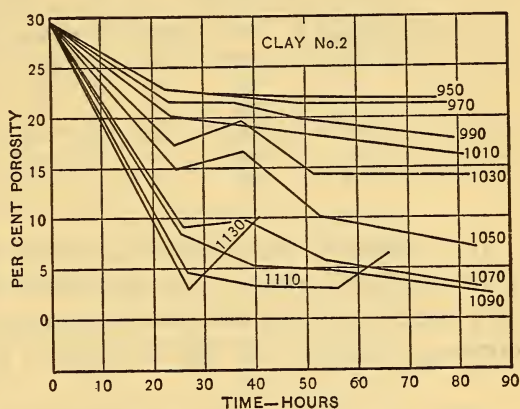


Fig. 7

TABLE 3

Clay No. 2 (Lab. No. 16)

[illegible]

Here some of the isoporosity equivalents are as follows:

Porosity	Tempera- ture reached	Time	Porosity	Tempera- ture reached	Time
Per cent	°	Hours	Per cent	°	Hours
20	990	49	7.5	1050	77
20	1010	24	7.5	1070	40
15	1030	45	7.5	1090	29
15	1050	24.5	4.5	1070	70
9	1050	62	4.5	1090	59
9	1070	26	4.5	1110	26.5

It is observed that overfiring occurs at 1130° after 41 and at 1110° after 66 hours. The maximum density is obtained after 86.5 hours at 1090°, and this temperature is the highest for safe burning, provided the rate of firing is not too slow. The effect

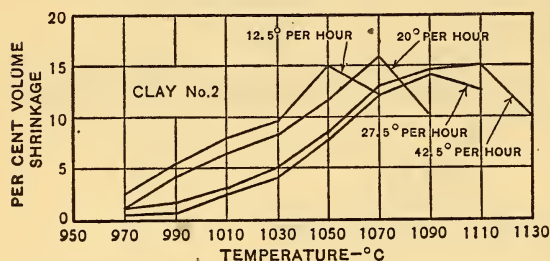


Fig. 8

of the speed of heating is brought out in the diagram of Fig. 8, in which the volume shrinkages are plotted. The point of maximum shrinkage is reached at 1050°, firing at the rate of 12.5° per hour; at 1070°, with a rise of 20° per hour; at 1090°, with 27.5° per hour; and at 1110°, with 42.5° per hour, thus verifying the statement that the slower the rate of firing the lower the temperature at which a given amount of heat work is accomplished. Attempts to work out a general relation between the rate of heating, temperature and porosity were unsatisfactory. Owing to the fact that the maximum shrinkages for the different rates of heating are sufficiently close together, corresponding to 15 ± 1 per cent, these values have been taken to be equivalent.

Plotting the rates of heating against the temperatures at which maximum shrinkage has been reached, the curve shown in Fig. 9 is obtained, which illustrates the relation of the maturing temperature to the rate of firing. Between the rates 12.5° and 27.5° per hour the temperature increases practically linearly; but

beyond 30° per hour the trend of the curve is toward a limiting value.

The speeds of vitrification at the different temperatures and rates of heating are presented in the diagram of Fig. 10, from which it is apparent that the maximum rate of condensation is obtained between 1050° to 1070°, with a rate of heating of 42.5° per hour.

(c) Clay No. 3.—Table 4 contains the values obtained in the porosity and shrinkage determinations, which are shown graphically in Figs. 11 and 12.

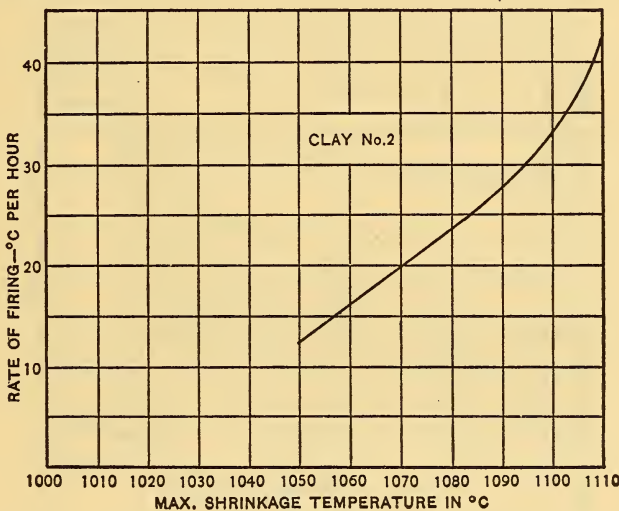


Fig. 9

TABLE 4
Clay No. 3. (Lab. No. 35)

Temperature reached, °C	Rate of heating, °C per hour							
	50.0	25.0	16.66	12.5	50.0	25.0	16.66	12.5
	Per cent porosity				Per cent volume shrinkage			
1050.....	21.4	21.6	20.0	18.9	18.1	18.4	21.1	20.3
1070.....	20.9	15.2	12.7	14.6	18.9	23.3	25.2	24.2
1090.....	16.8	11.8	9.7	23.0	26.9	28.1	27.5
1110.....	11.8	8.2	4.5	3.5	26.8	29.0	29.4	28.5
1130.....	6.8	2.5	1.1	0.7	28.0	29.1	29.3	28.0
1150.....	5.8	0.3	0.6	0.7	29.0	28.7	27.5	26.4
1170.....	2.8	0.8	22.1	2.7	25.0	25.5	18.2	20.9
1190.....	11.2	12.9	17.8	18.0	12.4	18.7

Some of the iso-porosity relations are as follows:

Porosity	Tempera- ture reached	Time	Porosity	Tempera- ture reached	Time
Per cent	°	Hours	Per cent	°	Hours
14	1090	43.5	5	1110	64
14	1110	22	5	1130	33
10	1090	61	5	1150	26.5
10	1110	34	3	1130	43.5
7	1110	52	3	1150	35
7	1130	22.5	3	1170	23.5

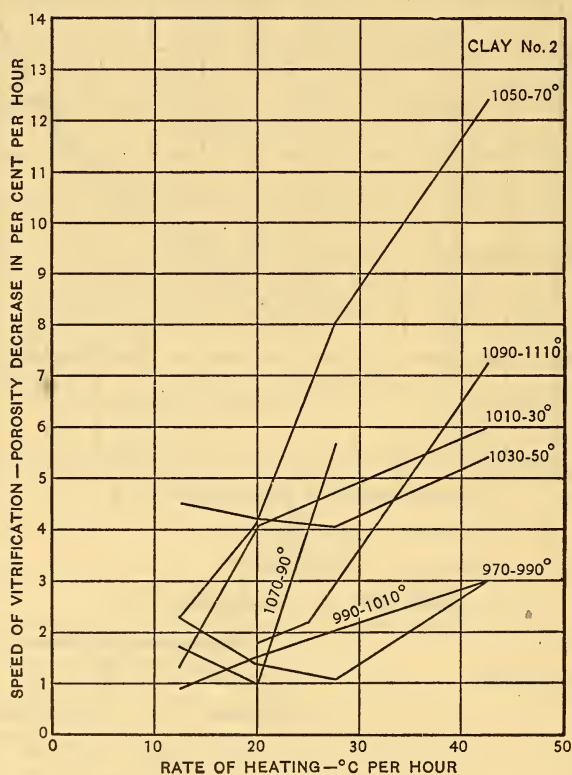


Fig. 10

That 1170° is too high a finishing temperature is shown by the fact that vesicular structure is produced when the firing is carried on at a rate so that this temperature is reached after 47

hours. The excellent firing behavior of this shale is shown by the steady decrease in porosity indicated by the 1130° and 1150° curves and the long range during which the minimum porosity is maintained. Incidentally, the fact is brought out that in the testing of clays the time of burning should not be too short even for small specimens. The rapid tests frequently made in such work are for this reason open to criticism. The longer the time of burning is taken so that it approaches the rates of commercial kiln operation the more useful will be the results obtained with reference to their industrial application. The diagram of Fig. 11

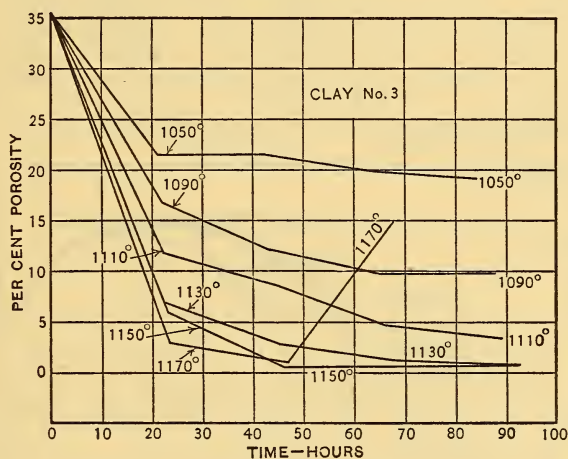


Fig. 11

shows also that complete vitrification is reached at 1130° and at 1150°, the difference being only the somewhat longer time required with the lower temperature. From the diagram of Fig. 12 it appears that the points of maximum shrinkage practically agree for the rates of heating of 12.5, 16.66, and 25° per hour at 1110°, while for the 50° rate the same point is reached only at 1150°. The maximum speed of vitrification for this shale is reached with the heating rate of 50° per hour, between 1070 to 1090° and 1110 to 1130°, and corresponds to 10.25 per cent porosity per hour.

(d) Clay No. 4.—The numerical data relating to the porosity and shrinkage determinations are compiled in Table 5, and the graphical presentation is given in Figs. 13 and 14.

TABLE 5
Clay No. 4. (Lab. No. 37)

Temperature reached, °C	Rate of heating, °C per hour							
	50.0	25.0	16.66	12.5	50.0	25.0	16.66	12.5
	Per cent porosity				Per cent volume shrinkage			
1030.....	30.7	28.8	29.0	5.0	8.7	6.1
1050.....	30.1	23.9	24.0	22.2	7.0	13.0	13.4	15.1
1070.....	22.4	18.8	13.4	14.4	14.8	19.0	19.6	22.4
1090.....	21.3	10.9	8.0	10.2	15.8	24.6	25.8	26.3
1110.....	9.9	8.2	4.5	4.0	24.8	27.4	27.2	27.2
1130.....	7.6	2.0	.1	.9	27.0	26.1	25.2	25.3
1150.....	3.2	1.0	2.3	4.4	26.1	24.4	17.7	19.7
1170.....	3.4	1.9	28.5	24.3	17.3	16.9
1190.....	24.3	31.4

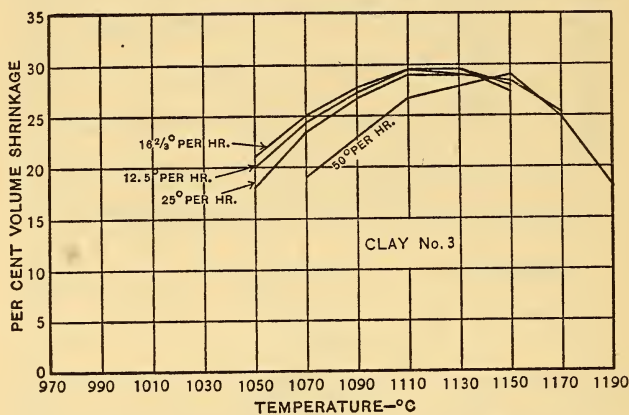


Fig. 12

A number of the isoporosity values are collected as follows:

Porosity	Temperature reached	Time	Porosity	Temperature reached	Time
Per cent	°	Hours	Per cent	°	Hours
20	1070	36	9.75	1110	22
20	1090	24.5	7.5	1110	49
15	1070	58	7.5	1130	23.5
15	1090	35	5	1110	63.5
9.75	1090	51	5	1130	34.0

Both the 1150° and 1170° curves show evidence of overburning. As with the preceding clay, the point of maximum shrinkage (Fig. 14) coincides for three rates of heating, but is 20° higher on

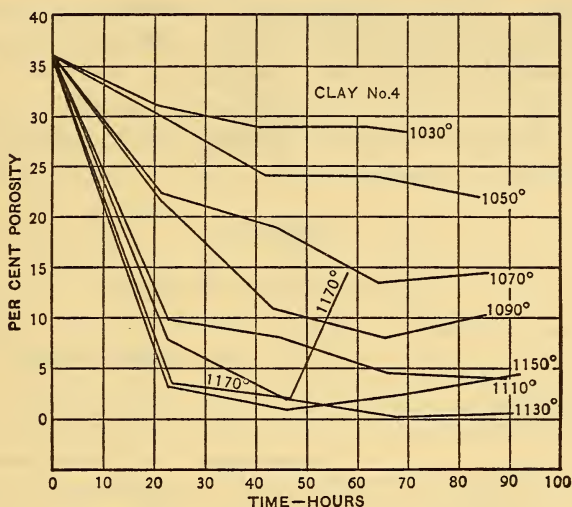


Fig. 13

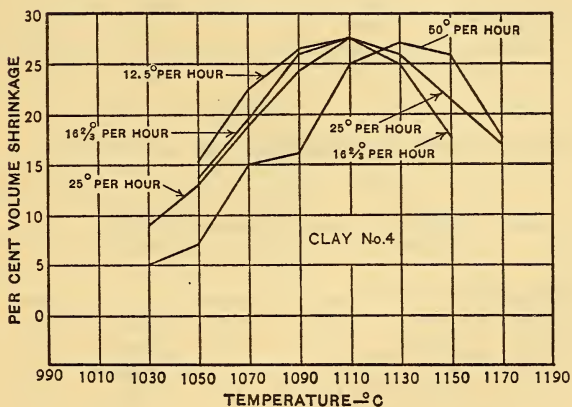


Fig. 14

the 50° curve. From this it appears that the rate of firing could be at least 25° per hour without displacing the point of maximum shrinkage.

The maximum safe burning temperature is about 1130°. The speed of vitrification was calculated to be 28.4 per cent porosity decrease per hour between 1090 and 1110°, for the heating rate of 50° per hour. With a temperature increase of 25° per hour the maximum speed of vitrification, 9.8 per cent porosity decrease per hour, is obtained between 1070 to 1090°.

(e) Clay No. 5.—Table 6 contains the porosity and shrinkage values obtained for this material which are reproduced diagrammatically in Figs. 15 and 16.

TABLE 6
Clay No. 5 (Lab. No. 14)

Temperature reached, °C	Rates of heating, °C per hour							
	50.0	25.0	16.66	12.5	50.0	25.0	16.66	12.5
	Per cent porosity				Per cent volume shrinkage			
990.....	41.3	40.2	39.9	41.9	1.5	1.1	1.8	1.3
1010.....	41.0	40.3	39.7	42.0	1.7	2.2	1.4	0.7
1030.....	40.6	38.4	36.4	38.8	2.5	3.3	3.3	3.2
1050.....	38.1	36.3	31.9	31.1	5.5	7.9	8.5	13.2
1070.....	33.1	5.4	.0	0.4	10.5	30.0	33.6	32.9
1090.....	4.6	0.2	.0	.0	30.3	33.8	30.3	32.0
1110.....	.0	0.2	.0	.0	31.1	27.9

Some of the iso-porosity relations are as follows:

Porosity	Temperature reached	Time	Porosity	Temperature reached	Time
Per cent	°	Hours	Per cent	°	Hours
37.5	1030	49	4.5	1070	46
37.5	1050	28	4.5	1090	22
32.5	1050	60	2.5	1070	54
32.5	1070	22	2.5	1090	32.5

The diagram of Fig. 15 shows strikingly the typical behavior of calcareous clays in which vitrification takes place rapidly and a short temperature interval separates the open from the dense

structure. This example illustrates also the influence of the composition upon the time-temperature relation and proves the impossibility of calculating a factor which does not take into account the specific decrease in viscosity due to the material itself.

Upon inspection of Fig. 16 it is noted that this clay is influenced appreciably by the rate of firing. While the maximum shrinkage points of the curves representing the 12.5° and 16.6° per hour rates coincide at 1070°, the corresponding point of the 25° curve is found to be at 1090° and of the 50° rate at 1110°.

Calculating the speed of vitrification in per cent porosity decrease per hour, the maximum value was

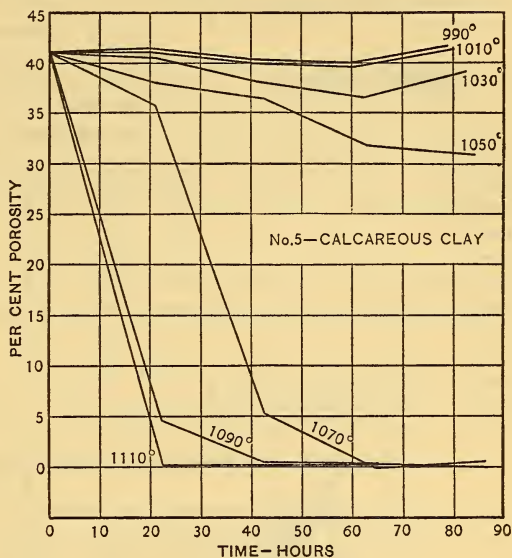


Fig. 15

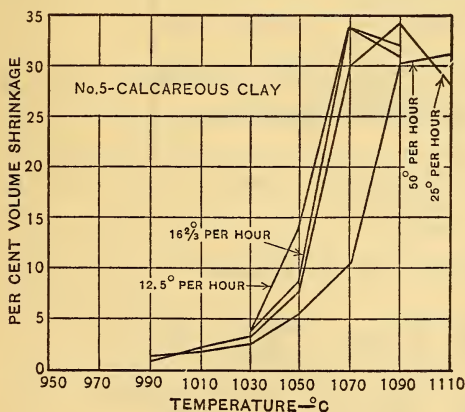


Fig. 16

found with the heating rate of 50° per hour and corresponded to 71 per cent between 1070 to 1090°, thus illustrating the rapidity of contraction. During the temperature interval 1050 to 1070° the maximum speed was found in connection with the 25° rate and amounted to 38.2 per cent.

(f) Clay No. 6.—Table 7 contains the numerical results obtained in connection

with this clay. The diagrams of Figs. 17 and 18 present these in graphical form.

TABLE 7
Clay No. 6 (Lab. No. 12)

Temperature reached, °C	Rates of heating, °C per hour							
	50.0	25.0	16.66	12.5	50.0	25.0	16.66	12.5
	Per cent porosity				Per cent volume shrinkage			
1030.....	24.5	23.3	23.6	23.6	12.0	13.3	12.8	12.8
1050.....	22.9	20.8	19.5	19.2	13.9	15.4	16.9	16.5
1070.....	22.6	17.9	15.1	16.8	15.5	19.1	18.1	18.9
1090.....	17.6	14.9	13.9	13.9	18.4	21.8	21.3	21.6
1110.....	16.2	12.8	9.3	9.5	20.9	23.9	24.8	23.7
1130.....	11.7	9.0	6.4	4.5	24.4	24.6	24.7	24.8
1150.....	8.1	5.5	1.2	.7	25.3	25.0	25.8	25.4
1170.....		1.5	1.3	.5		26.7	24.5	25.5
1190.....	1.5	0.5	1.6	.3	25.8	26.2	22.7	25.3
1210.....					24.9	25.3		24.1

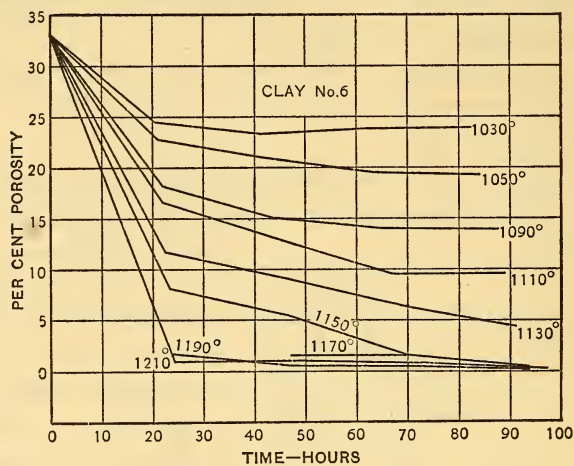


Fig. 17

Some of the isoporosity relations are as follows:

Porosity	Temperature reached	Time	Porosity	Temperature reached	Time
Per cent	°	Hours	Per cent	°	Hours
16	1090	35	10	1110	64
16	1110	25	10	1130	39
14	1090	61	8	1130	55
14	1110	38	8	1150	23
12	1110	50	5	1130	85
12	1130	25	5	1150	48

No evidence of overburning is shown, and the clay becomes dense without any apparent irregularities. For this reason this material may be burned safely with considerable rapidity to the temperature of 1170° and even higher.

The conditions therefore are almost ideal in this respect. It will also be noted that the progress of contraction is gradual, as is indicated by the regular intervals between the curves. A definite porosity limit is reached in the curves up to 1130° , showing that an equilibrium was obtained as far as the amount of softened material is concerned.

Referring to Fig. 18, the maximum shrinkage takes place at 1150° , with the rate of heating corresponding to 12.5° per hour;

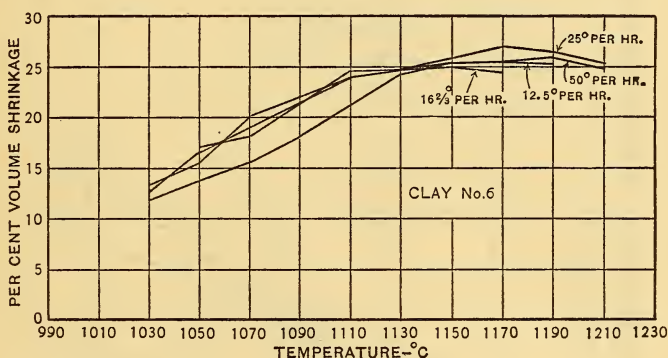


Fig. 18

a lower maximum contraction appears to have been reached at 1130° , with 16.6° per hour. The highest shrinkage—27 per cent—is obtained with the 25° rate. Singularly, the maximum contraction for the 50° rate is only 26 per cent, and is reached at 1190° . These differences, however, are not marked, and this clay more than the others responds to the time-temperature factor in a regular manner.

The diagram of Fig. 19 illustrates the speeds of vittrification, and it is apparent that the maximum speed is found in connection with the highest temperature interval and the highest rate. The other temperature intervals, however, do not arrange themselves in their order, a fact illustrating again the importance of

diverse factors. Regular dependence upon the temperature and rate of heating can exist only when the amount of softening material increases proportionally to the temperature increment. The fulfillment of this condition is quite improbable, since the fluxes, even though they dissolve silica and alumina to the possible limit, constantly produce new mixtures of varying viscosity, to say nothing of the physical obstacles encountered in bringing about solution. Hence the total quantity of softening material as well as its properties change more or less irregularly. The fact that

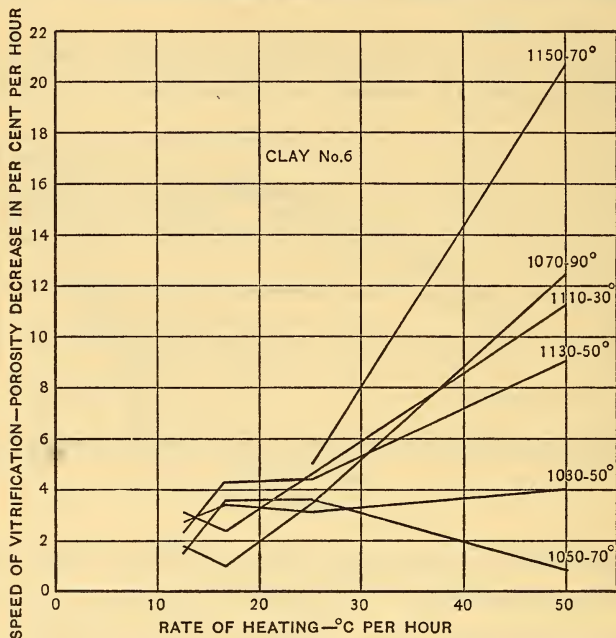


Fig. 19

vitrification is retarded toward the completion of vitrification is due in a large measure to the approach toward the final viscosity of the entire body.

4. CONE SOFTENING TEMPERATURES

In carrying out the burning experiments described at regular prescribed rates of heating an opportunity was offered to compare the softening temperatures of the cones with reference to the time

effect. The pyrometric cones used were of those manufactured by Prof. Edward Orton, Columbus, Ohio. It is a well-known fact that the silicate mixtures making up these pyrosopes do not possess definite melting points, but only a softening interval, and that the viscosity of the individual compositions is an important factor in determining the point at which the different numbers deform and bend. It is to be expected, therefore, that the time factor should affect the softening of the cones in a decided manner.

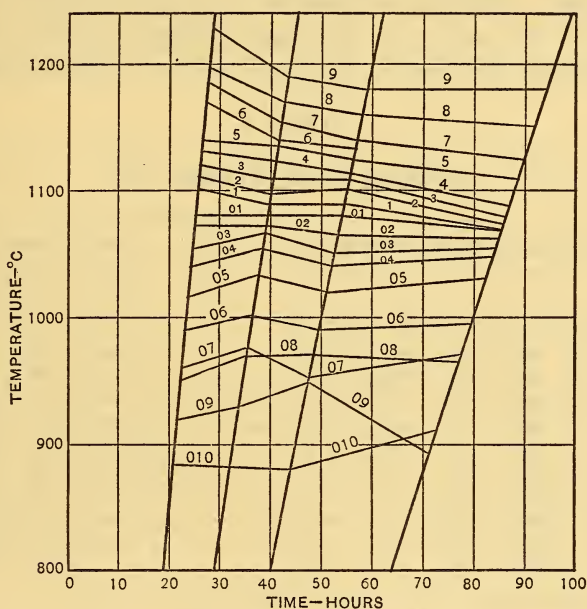


Fig. 20

In Table 8 the softening points of the cones used in the foregoing work are compiled with reference to the rate of heating. In Fig. 20 these data are presented graphically. Inspection of the latter shows at once the general tendency to connect high softening points with rapid heating, and vice versa. From cone 9 to 6, inclusive, the lowering of the deformation temperature is quite rapid at first and then slows down decidedly. While the softening point of cone 9 appears to remain constant for the slower rates of heating, it continues to become lower for the numbers 8,

7, and 6. Nos. 5 and 4 show a constant lowering of the point in question. With the introduction of ferric oxide in the composition irregularities begin to occur, although these are not marked until cone 03 is reached. Beginning with this number and with the increasing amount of boric acid entering into the mixtures, the effect of the heating rate becomes more and more irregular. Thus the rise in the softening temperature of cones 07 and 010 during the longer heating periods is manifestly due to the volatilization of boric acid. Reducing conditions or irregular firing can not be the cause of this behavior, since gas analysis showed a large air excess and since the supply of natural gas was under constant con-

TABLE 8
Softening Points of Cones, °C

Cone	Rate of heating, °C per hour				Cone	Rate of heating, °C per hour			
	42.5	27.5	20.0	12.5		42.5	27.5	20.0	12.5
010.....	885	885	880	910	1.....	1100	1085	1090	1070
09.....	920	930	950	890	2.....	1110	1090	1100	1075
08.....	950	970	970	965	3.....	1120	1110	1110	1080
07.....	960	975	950	970	4.....	1130	1125	1115	1090
06.....	990	1000	990	995	5.....	1140	1135	1125	1110
05.....	1015	1035	1025	1030	6.....	1170	1140	1135
04.....	1040	1055	1040	1045	7.....	1185	1155	1140	1125
03.....	1055	1065	1050	1050	8.....	1200	1170	1160	1150
02.....	1065	1070	1065	1060	9.....	1230	1190	1180	1190
01.....	1080	1080	1080	1070					

trol. Upon examination the cones also appeared to be of normal color and showed none of the vesicular structure due to flashing and reducing conditions.

The irregularity of the lower cone numbers is realized by the makers and users and evidently is connected with their composition. That the intervals between the iron carrying numbers differ so greatly from those between the higher members has not been generally recognized. As regards the higher numbers above No. 3, their regularity of softening and deforming is surprising, knowing the disadvantages under which such a system labors. The results pertaining to cones 03 and above have been checked repeatedly,

and invariably the softening occurs as is indicated by the curves. These facts should be applied in the use of the cones, as they certainly have been helpful in the work of this laboratory. Short burns necessitate the use of higher cone numbers than long burns in accomplishing the same result. Where at the same plant the rate of firing varies, difficulties are certain to be met with unless the proper corrections are made, as has been indicated.

Attention might also be called to the fact that the observed softening points do not agree with the approximate temperatures published and show wide differences.

5. SUMMARY

The effect of time in the firing of clay products is of great importance. A rapid rate of firing requires a higher finishing temperature than a slower one.

As a rule, the higher the content of fluxes the more marked will be the influence of the time factor.

It is impossible to work out general rules governing the time-temperature relations, owing to the fact that certain specific properties of the clays, such as their viscosity at kiln temperatures, vary widely according to the composition and physical structure of the different materials.

Six typical clays have been studied in this connection, and these results may serve as a guide in estimating the time effect upon similar clays.

Vesicular structure is produced not only by excessive temperature, but by longer continued burning at lower temperatures as well. The selection of a particular rate of burning must take into account the character of the clay and the size of the product to be fired. For most purposes the rates of firing should be between 10 to 35° C per hour.

The method of firing at a constant rate can not be applied to practical work. In conducting clay tests involving the use of specimens of the size used in this work a constant rate of heating from 30 to 35° per hour may be maintained after oxidation up to within about 40° of the minimum maturing temperature. From this point on a much slower rate, about 10° per hour, should be

employed until the burn is finished. In case reasonable uniformity of temperature can not be obtained in the kiln still another change is desirable, consisting in keeping the temperature constant at the minimum maturing point until the clay has reached the desired degree of density.

Unless the conditions of heating are stated, firing results of any kind lose much of their value.


The greater the tendency of a clay to produce vesicular structure the lower should be the burning temperature, with a corresponding increase in time. For this purpose it is necessary to know the temperature limits within which the time factor becomes effective. The speed of vitrification for a given clay, in general, is greatest at the highest temperature and the most rapid rate of heating. Probably 25° per hour is the maximum rate at which firing should take place under any conditions during vitrification.

The effect of the time-temperature relations should be studied closely for every clay, since only when reliable information concerning this subject is at hand is it possible to exercise complete control of the burning. The importance of such results applied in factory practice can not be emphasized too much.

The use of pyrometers in plant operation is to be urged most strongly, as they afford the only means of controlling the rate of firing. For the establishment of the end point of the burn pyrometric cones, shrinkage, and porosity determinations are of value.

In the use of cones the time factor should be taken into account.

WASHINGTON, May 20, 1913.



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